

NEW UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. 1.53(b))

Docket No.
M4065.0166/P166-A

Total pages in this
submission
63

TO THE ASSISTANT COMMISSIONER FOR PATENTS Box Patent Application Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

ACID BLEND FOR REMOVING ETCH RESIDUE

and invented by:

Kevin J. Torek and Donald L. Yates

IF A CONTINUATION APPLICATION, check appropriate box and supply requisite information:

- ☐ Continuation ☒ Divisional of Appln. Serial No. 09/342,243, filed June 29, 1999
☐ Continuation-in-part (CIP) of prior application No.: _____

Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below
2. ☒ Specification having 41 pages (plus title page) and including the following:
 - a. ☒ Descriptive title of the invention
 - b. ☐ Cross references to related applications (if applicable)
 - c. ☐ Statement regarding Federally-sponsored research/development (if applicable)
 - d. ☐ Reference to microfiche appendix (if applicable)
 - e. ☒ Background of the invention
 - f. ☒ Brief summary of the invention
 - g. ☒ Brief description of the drawings (if drawings filed)
 - h. ☒ Detailed description
 - i. ☒ Claims as classified below
 - j. ☒ Abstract of the disclosure

08/23/00
jc803 U.S. PTO

jc895 U.S. PTO
09/643946
06/23/00

09/643946 08/23/00

Application Elements (continued)

3. ☒ Drawing(s) (when necessary as prescribed by 35 U.S.C. 113)
☐ Formal ☒ Informal Number of sheets: 3
4. ☒ Oath or Declaration
 a. ☐ Newly executed (original or copy) ☐ Unexecuted
 b. ☒ Copy from a prior application (37 C.F.R. 1.63(d) (for continuation/divisional applications only)
 c. ☐ With Power of Attorney ☒ Without Power of Attorney
5. ☒ Incorporation by reference (usable if Box 4b is checked)
 The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6. ☒ The prior appln. is assigned to Micron Technology, Inc., Boise, Idaho (recorded June 29, 1999, Reel 010085/Frame 0450).
7. ☐ Genetic sequence submission (if applicable, all must be included)
 a. ☐ Paper copy
 b. ☐ Computer readable copy
 c. ☐ Statement verifying identical paper and computer readable copies

Accompanying Application

8. ☒ Assignment papers (*copy from prior appln. Serial No. 09/342,243*)
9. ☒ Power of Attorney and 37 C.F.R. 3.73(b) statement (*copy from prior appln. Serial No. 09/342,243*)
10. ☐ English translation document (*if applicable*)
11. ☒ Copy of Form PTO-1449 filed in prior appln. Serial No. 09/342,243
12. ☒ Preliminary Amendment
13. ☒ Acknowledgment postcard
14. ☐ Certified copy of priority document(s) (*if foreign priority is claimed*)
15. ☐ Certificate of Mailing
- ☐ First Class ☐ Express Mail (Label No.: _____)
16. ☐ Small Entity statement(s) -- # submitted (*if Small Entity status claimed*)

[illegible]

Accompanying Application (continued)

- 17.
- ☐
- Additional enclosures (please identify below):

Fee Calculation and Transmittal

The filing fee for this utility patent application is calculated and transmitted as follows:

☒ Large Entity ☐ Small Entity

CLAIMS AS FILED					
For	# Filed	# Allowed	# Extra	Rate	Fee
Total Claims	22	- 20 =	2	x \$18.00	\$36.00
Independent Claims	3	- 3 =	0	x \$78.00	
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					
Other Fees (specify purpose):					
BASIC FEE					\$690.00
TOTAL FILING FEE					\$726.00

☒ A check in the amount of \$726.00 to cover the total filing fee is enclosed.☒ The Commissioner is hereby authorized to charge Deposit Account No. 4 - 1073 as described below. A duplicate copy of this sheet is enclosed.☐ Charge the amount of _____ as filing fee.☒ Credit any overpayment.☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.31(b).

Dated: August 21, 2000

Thomas J. D'Amico
Attorney Reg. No. 28,371
Dickstein Shapiro Morin & Oshinsky LLP
2101 L Street NW
Washington, DC 20037-1526
(202) 785-9700

PATENT

Docket No.: M4065.0166/P166-A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Kevin J. Torek et al.

Serial No.: Not Yet Assigned
(Divisional of 09/342,243)

Prior Group Art Unit: 1765

Filed: Concurrently Herewith

Prior Examiner: L. Vinh

For: ACID BLEND FOR REMOVING
ETCH RESIDUE

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to examination on the merits, please amend the above-identified U.S. patent application as follows:

In the Specification:

Page 1, after the title, insert the following new paragraph:

--This application is a divisional of copending application Serial No. 09/342,243, filed June 29, 1999 and as such claims priority to the copending application.--.

Serial No.: Not Yet Assigned

Docket No.: M4065.0166/P166-A

In the Claims:


Please cancel claims 1-141.

REMARKS

This Preliminary Amendment is being filed together with a divisional application. Allowance of the application with claims 142-163 is respectfully requested.

Dated: August 21, 2000

Respectfully submitted,

By 
Thomas J. D'Amico
Registration No. 28,371
Salvatore P. Tamburo
Registration No. 45,153
DICKSTEIN SHAPIRO MORIN &
OSHINSKY LLP
2101 L Street NW
Washington, DC 20037-1526
(202) 785-9700

Attorneys for Applicants

03:23:00 " 3454960

Docket No.: M4065.166/P166
Micron Ref.: 98-0618; 98-0735

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR U.S. LETTERS PATENT

Title:

ACID BLEND FOR REMOVING ETCH RESIDUE

Inventors:

Kevin J. Torek
Donald L. Yates

Dickstein Shapiro Morin &
Oshinsky LLP
2101 L Street, N.W.
Washington, D.C. 20037
(202) 785-9700

ACID BLEND FOR REMOVING ETCH RESIDUE

FIELD OF THE INVENTION

The present invention relates to the fabrication of semiconductor devices and more particularly to a method for cleaning a semiconductor substrate after the formation of dry etch residues thereon.

BACKGROUND OF THE INVENTION

The importance of minimizing contamination during semiconductor fabrication processes has been recognized since the early days of the industry. As semiconductor devices have become smaller and more complex, cleanliness requirements have become increasingly stringent, especially for devices with submicron critical dimensions, because the ability to reliably create multi-level metallization structures is increasingly vital. The importance of cleaning and conditioning steps during the device fabrication process is also emphasized because small-scale residues that may not have seriously affected the performance of devices with large geometries may result in disabling defects in submicron devices.

Dry etch processes play a key role in developing multi-level metallization structures on semiconductor substrates. The step of transferring the desired pattern from the photoresist into the substrate is often accomplished via a dry etch process. While dry etch processes are effective for selectively etching the substrate in only the areas not masked by photoresist, these processes have a tendency to leave behind residues on the substrate. Although these residues may serve a beneficial role during a dry etch process, they are undesirable after the completion of the dry etch process. In back end of the line processes, where both dielectrics, such as SiO_2 , and metals, such as Al or W, are present, the residues left behind by dry etch processes may include both

organometallic and organosilicate species. These undesirable post-etch residues are often difficult to remove without damaging the desired substrate features.

Current methods for removing dry etch residues have met with only limited success. Traditional cleans involving aqueous acid solutions can not provide a general solution for removing these residues, as these processes are not suitable for processing in the presence of metal lines. Current strategies often involve treating substrates with solutions containing hydroxylamine (NH_2OH) and an organic chelating agent. These methods have shown some effectiveness but have significant drawbacks. These types of solutions can cause corrosion of exposed metal on the wafer and usually require long processing times at temperatures near 100 C. These hydroxylamine solutions are also expensive, as the chemicals are not only expensive to purchase but also typically require specialized disposal.

As the removal of dry etch residues grows increasingly troublesome in microelectronic device manufacture, there is a need for an effective method of removal of these residues which can be easily implemented in standard wafer processing equipment and has reduced costs for chemical purchase and disposal.

SUMMARY OF THE INVENTION

The present invention provides an adaptable method for removing organometallic, organosilicate, and other residues from a semiconductor substrate following a dry etch process. A substrate previously subjected to a dry etch process is exposed to a conditioning solution to remove residues remaining after the dry etch. The composition of the conditioning solution can be varied to match specific applications. The conditioning solution generally contains a source of fluorine, a complementary acid, a non-aqueous solvent, and preferably a surface passivation agent. One group of preferred conditioning solutions are

solutions composed of HF, H₃PO₄, a polyhydric alcohol such as propylene glycol, and a surface passivation agent such as citric acid. In an alternate group of preferred embodiments the conditioning solutions are composed of HF, HCl, a polyhydric alcohol, and a surface passivation agent. The substrate is exposed to the conditioning solution for a sufficient amount of time to remove the undesired residues. After exposing the substrate to the conditioning solution, the substrate is rinsed, preferably by exposing the substrate to a rinse bath of a mildly acidic aqueous solution. Preferably this rinse step also involves bubbling a gas through the rinse bath to agitate the rinse bath.

Additional advantages and features of the present invention will be apparent from the following detailed description and drawings which illustrate preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view of a substrate with dry etch residues near a sample device feature.

Figure 2 is a schematic cross-sectional view of a substrate undergoing the process of a preferred embodiment of the invention.

Figure 3 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 2.

Figure 4 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 3.

Figure 5 shows the substrate of Fig. 2 at a processing step subsequent to that shown in Fig. 4.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the following detailed description, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced.

5 These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that structural and chemical changes may be made without departing from the spirit and scope of the present invention.

10 The terms “wafer” and “substrate” are to be understood as including any semiconductor-based structure having an exposed layer which may be effectively cleaned by the process of the present invention. Typically this will include semiconductor-based structures which have been dry-etched and have resultant organometallic and/or organosilicate residues on an exposed layer, but other structures may also be beneficially treated by the present inventive method.

15 “Wafer” or “substrate” may include silicon-on-insulator (SOI) or silicon-on-sapphire (SOS) technology, doped and undoped semiconductors, epitaxial layers of silicon supported by a base semiconductor foundation, and other semiconductor structures. Furthermore, when reference is made to a “wafer” or “substrate” in the following description, previous process steps may have been

20 utilized to form regions or junctions in the base semiconductor structure or foundation. In addition, the semiconductor need not be silicon-based, but could be based on silicon-germanium, germanium, or gallium arsenide.

The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined by the appended

25 claims. When referring to solutions described herein, the term “percent” refers to the percent measured by weight, e.g., a 90% acetic acid solution is 90% by weight acetic acid.

Referring now to the drawings, where like elements are designated by like reference numerals, Fig. 1 depicts a semiconductor wafer 20 in an intermediate processing stage of a fabrication process. The wafer 20 comprises a substrate 22 with devices 24 located thereon. The devices 24 are covered by a dielectric layer 26 of SiO₂, BPSG, or other suitable material which has a top surface 28. A device feature that has been formed by a dry etch process is formed on the substrate 22, either on or in the dielectric layer 26. For exemplary purposes, the device feature will be illustrated and described as a trench 30, which may be a via, but it should be understood that the invention is not limited thereto.

The trench 30 is formed in the dielectric material, and has sidewalls 32 and a bottom surface 34. If trench 30 represents an unfilled via allowing connection between metal levels, the bottom surface 34 may be composed of a metal such as aluminum or tungsten. The wafer 20 of Fig. 1 has been subjected to a dry etch process followed by a photoresist ashing or stripping process. Due to the dry etch process, residues 40, which may be, for example, organosilicate or organometallic residues, are present on the top surface 28 of the dielectric layer 26 and on the sidewalls 32 of the trench 30. If not removed, the residues 40 could prevent proper deposition of subsequent layers in the trench 30 or on the dielectric layer 26.

An embodiment of the present invention for removing residues is illustrated by Figs. 2 through 5. This embodiment uses a conditioning solution to cleanse the substrate surface after performance of a dry etch. The substrate 22 is exposed to the conditioning solution for a period of time sufficient to remove residues 40 from the substrate surface while minimizing the amount of material removed from exposed surfaces, such as metal lines, vias, or dielectric layers. The composition of the conditioning solution can be varied to match specific

applications. The conditioning solution generally contains a fluorine source, a complementary acid, and a non-aqueous solvent. The complementary acid may be H_3PO_4 , HCl , or another acid or combination of acids which can serve as a pH suppressant. The non-aqueous solvent may be a polyhydric alcohol, such as propylene glycol or ethylene glycol. Alternatively, the non-aqueous solvent may be one of many other suitable organic solvents, including tetrahydrofuran, dimethylsulfoxide, propylene carbonate, or isopropyl alcohol. The conditioning solution preferably also contains a surface passivation agent. The surface passivation agent may be a carboxylic acid, such as citric acid, acetic acid, or EDTA. Other organic acids which are not carboxylic acids may also be suitable, such as ascorbic acid. Preferred conditioning solutions are solutions of HF , H_3PO_4 , and a polyhydric alcohol such as propylene glycol; solutions of HF , H_3PO_4 , a polyhydric alcohol, and a surface passivation agent; solutions of HF , HCl , and a polyhydric alcohol; and solutions of HF , HCl , a polyhydric alcohol, and a surface passivation agent such as citric acid.

Although HF is the preferred fluorine source, other fluorine sources may be effectively employed within the scope of this invention. For example, NH_4F might be employed as the fluorine source as long as the NH_4F was compatible with the other components selected for the conditioning solution. Similarly, H_3PO_4 is not the only source of phosphate contemplated within the inventive method. For example, phosphate salts which could dissociate to yield H_2PO_4^- , HPO_4^{2-} , or PO_4^{3-} might be appropriate depending on the other components in the conditioning solution. HF and H_3PO_4 , however, are particularly preferred and convenient choices for the fluorine source and the complementary acid.

Referring to Fig. 2, the process of the present invention begins subsequent to the formation of devices 24, which may be transistors, capacitors,

word lines, bit lines, or the like, on a substrate 22 of a wafer 20 and the formation of a dielectric layer 26 on the substrate 22. The dielectric layer 26 may be a silicon dioxide, borophosphosilicate glass (BPSG), phosphosilicate glass (PSG), borosilicate glass (BSG) or other dielectric layer, and may be deposited by chemical vapor deposition or other suitable means.

Fig. 3 depicts the next step of the process, in which a photoresist 42 is formed on the top surface 28 of the dielectric layer 26 by suitable means such as a spin-on technique. The photoresist 42 is patterned and developed, and a dry etch process is performed on the substrate using the patterned photoresist as an etch mask. At the end of the dry etch process, residues 40 are left behind on the substrate. Figure 4 depicts two possible locations where the residues might reside on the substrate once the remaining photoresist is removed by a suitable process such as ashing or stripping. Residues 40 might remain on the top surface 28 of the dielectric layer 26, or inside the trench 30, as shown in Fig. 4, or potentially at other locations on the wafer.

The wafer 20 is then subjected to the cleansing process of the present invention. The wafer 20 is exposed to a conditioning solution by any suitable method, which is typically a wet processing method. Suitable methods may involve immersion of the wafer 20, either singly or in combination with other wafers, into a bath containing the conditioning solution, or by dispensing of the conditioning solution onto one or more wafers 20 as a stream or spray, so long as such dispensing of the conditioning solution results in exposure of the surface of the substrate to the conditioning solution for the desired length of time. Other methods of treating substrates with the conditioning solution will be apparent to those skilled in the art. The wafer 20 is exposed to the conditioning solution for a time sufficient to remove residues 40 from the top surface 28 of the dielectric layer 26 and from the sidewalls 32 and bottom surface 34 of the

trench 30. Residues 40 may be organometallic residues, organosilicate residues, other post-etch residues, or a combination of these residues. The cleansing method of this invention is effective for removal of these residues when present individually or in combination.

5 The wafer 20 may then be rinsed to prepare the substrate for a subsequent process step. In one embodiment, the substrate is rinsed with deionized water. In a preferred embodiment, the substrate may be exposed to an acidic rinse composed of an aqueous solution of a suitable acid. Carboxylic acids such as citric acid, acetic acid, or EDTA (ethylene diamine tetraacetic acid) are preferred for this embodiment. Other organic acids which are not carboxylic acids may also be used, such as ascorbic acid.

10 In another embodiment, the aqueous acid solution may be buffered to raise the pH of the solution to any desired pH level up to approximately pH 8. In yet another embodiment, anti-etch agents may be added to the rinse bath, such as ammonium lactate or boric acid. In another embodiment, the substrate may be rinsed by exposing the wafer to an organic solvent, such as an alcohol, a polyhydric alcohol (such as propylene glycol), a ketone, or a fluorocarbon. In another embodiment, the rinse may be carried out in a bath and the rinse bath may be agitated by introduction of a gas. The agitating gas may be CO₂, N₂, or other gases which can be conveniently introduced into the rinse bath for agitation. In yet another embodiment, the solution may be agitated using megasonic energy. In still another embodiment, the solution may be agitated by manual or robot-controlled shaking of the vessel containing the rinse bath.

25 Use of the acidified rinse or buffered rinse greatly reduces the potential for unwanted consumption of the desired substrate materials after exposing the wafer to the conditioning solution. In embodiments where rinsing

is accomplished with a rinse bath, a gas may be bubbled through the rinse bath. When the gas is CO₂, introduction of the gas provides another means for acidifying the rinse water as well due to the formation of carbonic acid. When the rinse is already acidified, however, inert gases such as N₂ exhibit similar effectiveness to CO₂. In some applications of this method, either the wafer may not be susceptible to the unwanted consumption of the substrate or additional loss of substrate material may not be critical. In these cases the wafer may be rinsed with deionized water.

In still another embodiment, the wafer 20 may be pre-rinsed with a non-aqueous solvent prior to the rinse step. In one embodiment, the non-aqueous solvent is a polyhydric alcohol, such as propylene glycol. In another embodiment, the wafer is pre-rinsed with the same non-aqueous solvent used in the conditioning solution. After pre-rinsing the wafer with a non-aqueous solvent, the wafer may be rinsed with any of the rinses described above.

The exact nature and length of the rinse step may vary depending on the next process step the substrate will undergo. The wafer 20 may be spin-dried after rinsing, if appropriate. The final structure of the wafer 20 with the residue removed is shown in Fig. 5. Further steps to create a functional circuit from the wafer 20 may now be carried out.

Typically the conditioning solution is composed of a fluorine source, a complementary acid, a non-aqueous solvent, and a surface passivation agent. The fluorine source may be HF, NH₄F, or other suitable chemicals which can act as fluorine sources in the conditioning solution. The non-aqueous solvent is typically a polyhydric alcohol, such as propylene glycol or ethylene glycol. Other organic solvents may also be used, such as tetrahydrofuran, dimethylsulfoxide, propylene carbonate, or isopropyl alcohol. In many embodiments, propylene

glycol is preferred due to considerations of low health exposure risk and ease of disposal. Blends of more than one alcohol may also be used. The complementary acid may be H_3PO_4 , HCl , or another acid or combination of acids which may act as a pH suppressant. Preferably, the acid or combination of acids selected as the pH suppressant should be able to reduce the pH of the solution to below pH 2. The surface passivation agent is typically a carboxylic acid. Preferred carboxylic acids include citric acid, acetic acid, or EDTA. Other organic acids which are not carboxylic acids may also be used, such as ascorbic acid. Other surface passivation agents will be apparent to those skilled in the art. Other surface passivation agents could generally include chelants or reducing agents.

In one series of embodiments, the conditioning solution is composed of HF as the fluorine source, propylene glycol as the non-aqueous solvent, H_3PO_4 as the complementary acid, and citric acid as the surface passivation agent. In one embodiment, the conditioning solution is composed of approximately 0.01 percent to approximately 5.0 percent HF, approximately 80 percent to approximately 95 percent propylene glycol, approximately 1 percent to approximately 15 percent H_3PO_4 , and approximately 0.001 percent to approximately 1.0 percent citric acid. In a preferred embodiment, the conditioning solution is composed of approximately 0.25 percent to approximately 0.3 percent HF, approximately 89 percent to approximately 94 percent propylene glycol, approximately 6 percent to approximately 7 percent H_3PO_4 , and approximately 0.09 percent to approximately 0.50 percent citric acid. In a particularly preferred embodiment, the conditioning solution is composed of approximately 0.27 percent HF, approximately 91.5 percent propylene glycol, approximately 6.5 percent H_3PO_4 , and approximately 0.25 percent citric acid.

In the above conditioning solutions the balance of the solution weight is made up by water. In many embodiments the conditioning solution is prepared by combining stock acid solutions which contain water, so a small amount of water may be present in the conditioning solution. It is preferred, however, that the water content of the conditioning solution be as low as possible.

In another series of embodiments, the conditioning solution is prepared by choosing HF as the fluorine source, HCl as the complementary acid, propylene glycol as the non-aqueous solvent, and citric acid as the surface passivation agent. In an embodiment, the conditioning solution is composed of approximately 0.01 percent to approximately 5.0 percent HF, approximately 80 percent to approximately 99 percent propylene glycol, approximately 0.003 percent to approximately 1.0 percent HCl, and approximately 0.001 percent to approximately 1.0 percent citric acid. In a preferred embodiment, the conditioning solution is composed of approximately 0.25 percent to approximately 0.3 percent HF, approximately 90 percent to approximately 98 percent propylene glycol, approximately 0.005 percent to approximately 0.009 percent HCl, and approximately 0.09 percent to approximately 0.5 percent citric acid. In a particularly preferred embodiment, the conditioning solution is composed of approximately 0.27 percent HF, approximately 97.5 percent propylene glycol, approximately 0.006 percent HCl, and approximately 0.25 percent citric acid.

Once again, the balance of the solution weight in the above conditioning solutions is made up by water. In many embodiments, the conditioning solution is prepared by combining stock acid solutions which contain water, so a small amount of water may be present in the conditioning

solution. It is preferred, however, that the water content of the conditioning solution be as low as possible.

In another series of embodiments, the surface passivation agent may be omitted from the conditioning solution. The conditioning solution will still effectively remove any organometallic, organosilicate, and other post-etch residues if the surface passivation agent is omitted. In these embodiments, however, the risk of damage to features on the surface of the substrate is substantially increased. While these embodiments may be effectively employed, greater care must be taken with other reaction parameters such as processing time and temperature in order to avoid potential damage to desired surface features or the substrate.

Residue removal with the conditioning solution may be performed at temperatures of approximately 5 to approximately 60 degrees Celsius. Temperatures below 5 degrees Celsius may be used, but are not as favorable due to decreased residue removal speeds. As a result, at lower temperatures the conditioning solution may need to be applied to the substrate for longer periods of time, leading to lower throughput in a production setting. Temperatures above 60 degrees Celsius may also be used. Preferably, the substrate is exposed to the conditioning solution at a temperature of approximately 35 to approximately 40 degrees Celsius. Exposing the substrate to the conditioning solution at a temperature of approximately 38 degrees Celsius is a particularly preferred embodiment of this invention.

Preferably, the substrate is exposed to the conditioning solution for a period of time sufficient to remove any undesirable dry etch residues from the surface of the substrate. This may involve an exposure of the substrate to the conditioning solution for periods of time ranging from about 10 seconds to

about 60 seconds or longer depending on the exact nature of the substrate and the process temperature. Longer exposure times, such as about 180 seconds or longer, allow for greater removal efficiency of the dry etch residues but will also lead to lower throughput in a production setting. Also, depending on the exact nature of the substrate, longer exposures to the conditioning solution may eventually lead to removal of material from exposed features on the surface of the substrate, such as metal lines, vias, or dielectric surfaces. As a result, the optimal amount of time for exposure of a substrate to the conditioning solution will be substrate dependent. The preferred exposure time could be near 10 seconds, near 60 seconds, near 180 seconds, or a longer or shorter period of time depending on the exact nature of the target substrate as well as the residues targeted for removal.

The substrate may be treated with the conditioning solution by immersing the substrate in a bath of the conditioning solution. Alternatively, the substrate may be treated with the conditioning solution by dispensing the solution on to the substrate, such as by a spray technique. Other methods for exposing the substrate to the conditioning solution will be apparent to those skilled in the art.

Without being bound by any particular theory, it is currently believed that several factors contribute to the effectiveness of this method for removing dry etch residues. It is believed that the carboxylic acid or other organic acid plays a role by passivating the surface of exposed metal lines, especially aluminum lines, which are on the surface of the substrate. In embodiments where the conditioning solution includes phosphoric acid, it is believed that the H_3PO_4 and HF play complementary roles of aiding in the removal of organometallic and organosilicate residues, respectively. In embodiments where a pH suppressant is present, it is believed that the low pH of the conditioning solution tends to allow

hydrofluoric acid present in the solution to exist as molecular HF and H_2F_2 , as opposed to undergoing dissociation into H^+ , F^- , HF^{2-} , or any of the other likely species produced when HF dissociates in solution. By preventing dissociation of the HF present in the conditioning solution, the HF is forced to remain in its molecular form which generally reacts much more slowly with substrate materials such as SiO_2 or the aluminum lines likely to be exposed on a substrate surface.

An alternate theory which could explain the lack of reactivity with the aluminum lines is that the nature of the conditioning solution suppresses the solubility of aluminum fluoride. Aluminum fluoride is one of the likely products of any reaction involving aluminum lines on the surface of the substrate. Lowering the solubility of aluminum fluoride might cause this reaction product to build up at the surface of the aluminum lines and prevent further reaction.

As can be seen from the embodiments described herein, the present invention encompasses processes of removing dry etch residues from substrates having exposed areas of metal and/or dielectric. In one embodiment the substrate is treated with/exposed to an conditioning solution composed of a fluorine source such as HF, a non-aqueous solvent, which is typically a polyhydric alcohol such as propylene glycol, a complementary acid, which could include H_3PO_4 , HCl, or other pH suppressants, and a surface passivation agent, which is typically a carboxylic acid such as citric acid. The conditioning solution efficiently removes organometallic, organosilicate, and other dry etch residues with minimal impact on exposed features on the substrate surface.

The above description and drawings are only illustrative of preferred embodiments which achieve the objects, features and advantages of the present invention. It is not intended that the present invention be limited to the illustrated embodiments. Any modification of the present invention which

comes within the spirit and scope of the following claims should be considered part of the present invention.

What is claimed as new and desired to be protected by Letters Patent
of the United States is:

5

[illegible]

1. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:

exposing a semiconductor substrate having dry etch residues thereon to a
5 conditioning solution, wherein the conditioning solution comprises a fluorine source, a
complementary acid, and a non-aqueous solvent.

2. The method of claim 1, wherein the fluorine source is HF.

3. The method of claim 1, wherein the fluorine source is NH_4F .

4. The method of claim 1, wherein the complementary acid is H_3PO_4 .

10 5. The method of claim 1, wherein the complementary acid is a phosphate
salt.

6. The method of claim 1, wherein the complementary acid is HCl.

7. The method of claim 1, wherein the complementary acid is a pH
suppressant.

15 8. The method of claim 1, wherein the non-aqueous solvent is a polyhydric
alcohol.

9. The method of claim 1, wherein the non-aqueous solvent is propylene glycol.

10. The method of claim 1, wherein the non-aqueous solvent is ethylene glycol.

11. The method of claim 1, wherein the non-aqueous solvent is tetrahydrofuran.

12. The method of claim 1, wherein the non-aqueous solvent is dimethylsulfoxide.

13. The method of claim 1, wherein the non-aqueous solvent is propylene carbonate.

14. The method of claim 1, wherein the non-aqueous solvent is isopropyl alcohol.

15. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is H_3PO_4 .

16. The method of claim 15, wherein the HF, propylene glycol, and H_3PO_4 are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 95 : 1 – 15.

17. The method of claim 15, wherein the HF, propylene glycol, and H_3PO_4 are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 89 – 94 : 6 – 7.

18. The method of claim 15, wherein the HF, propylene glycol, and H_3PO_4 are present in the conditioning solution in the approximate proportion of 0.27 : 91.5 : 6.5.

19. The method of claim 1, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, and the complementary acid is HCl.

20. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0.

21. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 93 – 98 : 0.005 – 0.009.

22. The method of claim 19, wherein the HF, propylene glycol, and HCl are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006.

23. The method of claim 1, wherein the conditioning solution further comprises a surface passivation agent.

24. The method of claim 23, wherein the surface passivation agent is a carboxylic acid.

5 25. The method of claim 23, wherein the surface passivation agent is citric acid.

26. The method of claim 23, wherein the surface passivation agent is acetic acid.

27. The method of claim 23, wherein the surface passivation agent is EDTA.

10 28. The method of claim 23, wherein the surface passivation agent is an organic acid.

29. The method of claim 23, wherein the surface passivation agent is ascorbic acid.

30. The method of claim 23, wherein the surface passivation agent is a
15 chelant.

31. The method of claim 23, wherein the surface passivation agent is a reducing agent.

32. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is H_3PO_4 , and the surface passivation agent is citric acid.

33. The method of claim 32, wherein the HF, propylene glycol, H_3PO_4 , and
5 citric acid are present in the conditioning solution in the approximate proportion of
0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

34. The method of claim 32, wherein the HF, propylene glycol, H_3PO_4 , and
citric acid are present in the conditioning solution in the approximate proportion of
0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.09 – 0.5.

35. The method of claim 32, wherein the HF, propylene glycol, H_3PO_4 , and
10 citric acid are present in the conditioning solution in the approximate proportion of
0.27 : 91.5 : 6.5 : 0.25.

36. The method of claim 23, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface
15 passivation agent is citric acid.

37. The method of claim 36, wherein the HF, propylene glycol, HCl, and
citric acid are present in the conditioning solution in the approximate proportion of
0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

38. The method of claim 36, wherein the HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion of 0.25 – 0.3 : 93 – 98 : 0.005 – 0.009 : 0.09 – 0.5.

39. The method of claim 36, wherein the HF, propylene glycol, HCl, and
5 citric acid are present in the conditioning solution in the approximate proportion of 0.27 : 97.5 : 0.006 : 0.25.

40. The method of claim 1, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

41. The method of claim 1, wherein said exposure step is performed at a
10 temperature within the range of approximately 35 to approximately 40 degrees Celsius.

42. The method of claim 1, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

43. The method of claim 1, wherein said exposure step further comprises immersing the substrate in the conditioning solution.

44. The method of claim 1, wherein said exposure step further comprises
15 dispensing the conditioning solution onto the substrate.

45. The method of claim 1, wherein said exposure step is performed for a time sufficient to remove substantially all dry etch residues from the substrate.

46. The method of claim 1, wherein said exposure step is performed for approximately 10 seconds or longer.

5 47. The method of claim 1, wherein said exposure step is performed for approximately 60 seconds or longer.

48. The method of claim 1, further comprising rinsing the substrate after said exposure step.

49. The method of claim 48, wherein said rinsing step comprises exposing the
10 substrate to deionized water.

50. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an aqueous acid solution.

51. The method of claim 50, wherein the aqueous acid solution is a solution of a carboxylic acid.

15 52. The method of claim 50, wherein the aqueous acid solution is a solution of citric acid.

53. The method of claim 50, wherein the aqueous acid solution is a solution of EDTA.

54. The method of claim 50, wherein the aqueous acid solution is a solution of acetic acid.

5 55. The method of claim 50, wherein the aqueous acid solution is a solution of an organic acid.

56. The method of claim 50, wherein the aqueous acid solution is a solution of ascorbic acid.

57. The method of claim 50, wherein the aqueous acid solution is a solution
10 of carbonic acid.

58. The method of claim 50, wherein the aqueous acid solution is buffered to a pH between approximately 4.0 and approximately 8.0.

59. The method of claim 48, wherein said rinsing step comprises exposing the substrate to an organic solvent.

15 60. The method of claim 59, wherein the organic solvent is propylene glycol.

61. The method of claim 48, wherein said rinsing step comprises exposing the substrate to a solution containing an anti-etch agent.

62. The method of claim 61, wherein the anti-etch agent is ammonium lactate.

63. The method of claim 61, wherein the anti-etch agent is boric acid.

64. The method of claim 48, wherein said rinsing step further comprises
5 immersing the substrate in a rinse bath.

65. The method of claim 64, wherein said rinsing step further comprises
agitating the rinse bath.

66. The method of claim 65, wherein the rinse bath is agitated with
megasonic energy.

67. The method of claim 65, wherein the rinse bath is agitated by bubbling a
10 gas through the rinse bath.

68. The method of claim 67, wherein CO₂ is bubbled through the rinse bath.

69. The method of claim 67, wherein N₂ is bubbled through the rinse bath.

70. The method of claim 48, further comprising pre-rinsing the substrate with
15 a non-aqueous solvent subsequent to said exposing step but prior to said rinsing step.

71. The method of claim 70, wherein the non-aqueous solvent is a polyhydric alcohol.

72. The method of claim 70, wherein the non-aqueous solvent is propylene glycol.

5 73. The method of claim 70, wherein the non-aqueous solvent is the same non-aqueous solvent used in the conditioning solution.

74. A method for removing dry etch residues from a semiconductor substrate comprising the steps of:

treating a semiconductor substrate having dry etch residues thereon with a
10 conditioning solution, wherein the conditioning solution comprises a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.

75. The method of claim 74, wherein the fluorine source is HF.

76. The method of claim 74, wherein the fluorine source is NH_4F .

77. The method of claim 74, wherein the non-aqueous solvent is a polyhydric
15 alcohol.

78. The method of claim 74, wherein the non-aqueous solvent is propylene glycol.

79. The method of claim 74, wherein the non-aqueous solvent is ethylene glycol.

80. The method of claim 74, wherein the non-aqueous solvent is tetrahydrofuran.

5 81. The method of claim 74, wherein the non-aqueous solvent is dimethylsulfoxide.

82. The method of claim 74, wherein the non-aqueous solvent is propylene carbonate.

83. The method of claim 74, wherein the non-aqueous solvent is isopropyl
10 alcohol.

84. The method of claim 74, wherein the complementary acid is H_3PO_4 .

85. The method of claim 74, wherein the complementary acid is a phosphate salt.

86. The method of claim 74, wherein the complementary acid is HCl .

15 87. The method of claim 74, wherein the complementary acid is a pH suppressant.

88. The method of claim 74, wherein the surface passivation agent is a carboxylic acid.

89. The method of claim 74, wherein the surface passivation agent is citric acid.

90. The method of claim 74, wherein the surface passivation agent is acetic acid.

91. The method of claim 74, wherein the surface passivation agent is EDTA.

92. The method of claim 74, wherein the surface passivation agent is an organic acid.

93. The method of claim 74, wherein the surface passivation agent is ascorbic acid.

94. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

95. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

96. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.09 – 0.5.

97. The method of claim 94, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

98. The method of claim 74, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is H_3PO_4 , and the surface passivation agent is citric acid.

99. The method of claim 98, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

100. The method of claim 98, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

101. The method of claim 98, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

102. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 90 percent non-aqueous solvent, approximately 1 percent to approximately 15 percent of the complementary acid, and approximately
5 0.001 to approximately 1.0 percent of the surface passivation agent.

103. The method of claim 74, wherein the conditioning solution is a solution composed of approximately 0.01 to approximately 5.0 percent of the fluorine source, approximately 80 to approximately 95 percent non-aqueous solvent, approximately 0.003 percent to approximately 1.0 percent of the complementary acid, and
10 approximately 0.001 to approximately 1.0 percent of the surface passivation agent.

104. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

105. The method of claim 74, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

15 106. The method of claim 74, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

107. The method of claim 74, wherein said exposure step is performed for a time sufficient to substantially remove all dry etch residues from the substrate.

108. The method of claim 74, wherein said exposure step is performed for approximately 60 seconds or longer.

109. The method of claim 74, further comprising rinsing the substrate after said exposure step.

5 110. A method for cleaning a wafer after a dry etch process comprising the steps of:

treating a wafer having at least one of organometallic and organosilicate residues on exposed surfaces of the wafer with a conditioning solution composed of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent
10 until the residues are removed from the wafer.

111. The method of claim 110, further comprising rinsing the substrate after said treating step.

112. The method of claim 110, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface
15 passivation agent is citric acid.

113. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

114. The method of claim 112, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

115. The method of claim 112, where HF, propylene glycol, HCl, and citric
5 acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

116. The method of claim 110, wherein the fluorine source is HF, the non-
aqueous solvent is propylene glycol, the complementary acid is H_3PO_4 , and the surface
passivation agent is citric acid.

10 117. The method of claim 116, where HF, propylene glycol, H_3PO_4 , and citric
acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 :
80 – 95 : 1 – 15 : 0.001 – 1.0.

118. The method of claim 116, where HF, propylene glycol, H_3PO_4 , and citric
acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 :
15 89 – 94 : 6 – 7 : 0.009 – 0.5.

119. The method of claim 116, where HF, propylene glycol, H_3PO_4 , and citric
acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 :
6.5 : 0.25.

120. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

121. The method of claim 110, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

5 122. The method of claim 110, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

123. The method of claim 110, wherein said exposure step is performed for approximately 60 seconds or longer.

124. A method for processing a substrate with patterned photoresist on the
10 substrate surface comprising the steps of:

providing a substrate with patterned photoresist on a surface of the substrate;

performing a dry etch process on the substrate;

removing any remaining photoresist from the surface of the substrate; and

15 exposing the substrate to a conditioning solution of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent.

125. The method of claim 124, further comprising rinsing the substrate after said exposure step.

126. The method of claim 124, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is HCl, and the surface passivation agent is citric acid.

127. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 99 : 0.003 – 1.0 : 0.001 – 1.0.

128. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 90 – 98 : 0.005 – 0.009 : 0.009 – 0.5.

129. The method of claim 126, where HF, propylene glycol, HCl, and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 97.5 : 0.006 : 0.25.

130. The method of claim 124, wherein the fluorine source is HF, the non-aqueous solvent is propylene glycol, the complementary acid is H_3PO_4 , and the surface passivation agent is citric acid.

131. The method of claim 130, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.01 – 5.0 : 80 – 95 : 1 – 15 : 0.001 – 1.0.

132. The method of claim 130, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.25 – 0.3 : 89 – 94 : 6 – 7 : 0.009 – 0.5.

133. The method of claim 130, where HF, propylene glycol, H_3PO_4 , and citric acid are present in the conditioning solution in the approximate proportion 0.27 : 91.5 : 6.5 : 0.25.

134. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 5 to approximately 60 degrees Celsius.

135. The method of claim 124, wherein said exposure step is performed at a temperature within the range of approximately 35 to approximately 40 degrees Celsius.

136. The method of claim 124, wherein said exposure step is performed at a temperature of approximately 38 degrees Celsius.

137. The method of claim 124, wherein said exposure step is performed for approximately 60 seconds or longer.

138. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the approximate ratio 0.01-5.0 : 80-95 : 0.003 – 1.0 : 0.001-1.0.

139. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, H₃PO₄, and citric acid in the approximate ratio 0.01-5.0 : 80-90 : 1-15 : 0.001-1.0.

140. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, HCl, and citric acid in the ratio 0.25 – 0.3 : 90-98 : 0.005 – 0.009 : 0.009-0.5; and rinsing the wafer.

141. A method for treating a semiconductor substrate to remove residues remaining after a dry etch process comprising the steps of:

exposing a substrate with at least one of organometallic and organosilicate residues on the substrate surface to a conditioning solution of HF, propylene glycol, H₃PO₄, and citric acid in the ratio 0.25 – 0.3 : 90-94 : 6-7 : 0.009-0.5; and rinsing the wafer.

142. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

hydrofluoric acid;

phosphoric acid;

propylene glycol; and

citric acid.

143. The solution of claim 142, wherein said solution consists essentially of hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid.

144. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 1-15 : 80 – 90 : 0.001 – 1.0.

145. The solution of claim 144, wherein said solution comprises approximately 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 1 to approximately 15 percent phosphoric acid, approximately 80 to approximately 95 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

146. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.25 – 0.3 : 6 – 7 : 90 – 94 : 0.009 – 0.5.

147. The solution of claim 146, wherein said solution comprises approximately 0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately 7 percent phosphoric acid, approximately 90 to approximately 94 percent propylene glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

5 148. The solution of claim 142, wherein said hydrofluoric acid, phosphoric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.27 : 6.5 : 91.5 : 0.25.

149. The solution of claim 148, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately 6.5 percent phosphoric acid,
10 approximately 91.5 percent propylene glycol, and approximately 0.25 percent citric acid.

150. A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process, said solution comprising:

hydrofluoric acid;

15 hydrochloric acid;

propylene glycol; and

citric acid.

151. The solution of claim 150, wherein said solution consists essentially of hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid.

152. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.01 – 5.0 : 0.003 – 1.0 : 80 – 99 : 0.001 – 1.0.

153. The solution of claim 152, wherein said solution comprises approximately
5 0.01 to approximately 5.0 percent hydrofluoric acid, approximately 0.003 to approximately 1.0 percent hydrochloric acid, approximately 80 to approximately 99 percent propylene glycol, and approximately 0.001 to approximately 1.0 percent citric acid.

154. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric
10 acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.25 – 0.3 : 0.005 – 0.009 : 90 – 98 : 0.009 – 0.5.

155. The solution of claim 154, wherein said solution comprises approximately
0.25 to approximately 0.3 percent hydrofluoric acid, approximately 6 to approximately
7 percent hydrochloric acid, approximately 90 to approximately 98 percent propylene
15 glycol, and approximately 0.009 to approximately 0.5 percent citric acid.

156. The solution of claim 150, wherein said hydrofluoric acid, hydrochloric acid, propylene glycol, and citric acid are present in said solution in the approximate proportion of 0.27 : 0.006 : 97.5 : 0.25.

157. The solution of claim 156, wherein said solution comprises approximately 0.27 percent hydrofluoric acid, approximately 0.006 percent hydrochloric acid, approximately 97.5 percent propylene glycol, and approximately 0.25 percent citric acid.

5 ~~158.~~ A solution for use in removing residues remaining on a semiconductor substrate after a dry etch process consisting essentially of a fluorine source, a complementary acid, and a non-aqueous solvent.

159. The solution of claim 158, wherein the fluorine source is hydrofluoric acid, the complementary acid is phosphoric acid, and the non-aqueous solvent is
10 propylene glycol.

160. The solution of claim 158, wherein the fluorine source is hydrofluoric acid, the complementary acid is hydrochloric acid, and the non-aqueous solvent is propylene glycol.

161. The solution of claim 158, wherein said solution further includes a surface
15 passivation agent.

162. The solution of claim 161, wherein the fluorine source is hydrofluoric acid, the complementary acid is phosphoric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.

163. The solution of claim 161, wherein the fluorine source is hydrofluoric acid, the complementary acid is hydrochloric acid, the non-aqueous solvent is propylene glycol, and the surface passivation agent is citric acid.

1. **Introduction**
 2. **Background**
 3. **Methodology**
 4. **Results**
 5. **Discussion**
 6. **Conclusion**
 7. **References**
 8. **Appendix**
 9. **Figure 1**
 10. **Figure 2**
 11. **Figure 3**
 12. **Figure 4**
 13. **Figure 5**
 14. **Figure 6**
 15. **Figure 7**
 16. **Figure 8**
 17. **Figure 9**
 18. **Figure 10**
 19. **Figure 11**
 20. **Figure 12**
 21. **Figure 13**
 22. **Figure 14**
 23. **Figure 15**
 24. **Figure 16**
 25. **Figure 17**
 26. **Figure 18**
 27. **Figure 19**
 28. **Figure 20**
 29. **Figure 21**
 30. **Figure 22**
 31. **Figure 23**
 32. **Figure 24**
 33. **Figure 25**
 34. **Figure 26**
 35. **Figure 27**
 36. **Figure 28**
 37. **Figure 29**
 38. **Figure 30**
 39. **Figure 31**
 40. **Figure 32**
 41. **Figure 33**
 42. **Figure 34**
 43. **Figure 35**
 44. **Figure 36**
 45. **Figure 37**
 46. **Figure 38**
 47. **Figure 39**
 48. **Figure 40**
 49. **Figure 41**
 50. **Figure 42**
 51. **Figure 43**
 52. **Figure 44**
 53. **Figure 45**
 54. **Figure 46**
 55. **Figure 47**
 56. **Figure 48**
 57. **Figure 49**
 58. **Figure 50**
 59. **Figure 51**
 60. **Figure 52**
 61. **Figure 53**
 62. **Figure 54**
 63. **Figure 55**
 64. **Figure 56**
 65. **Figure 57**
 66. **Figure 58**
 67. **Figure 59**
 68. **Figure 60**
 69. **Figure 61**
 70. **Figure 62**
 71. **Figure 63**
 72. **Figure 64**
 73. **Figure 65**
 74. **Figure 66**
 75. **Figure 67**
 76. **Figure 68**
 77. **Figure 69**
 78. **Figure 70**
 79. **Figure 71**
 80. **Figure 72**
 81. **Figure 73**
 82. **Figure 74**
 83. **Figure 75**
 84. **Figure 76**
 85. **Figure 77**
 86. **Figure 78**
 87. **Figure 79**
 88. **Figure 80**
 89. **Figure 81**
 90. **Figure 82**
 91. **Figure 83**
 92. **Figure 84**
 93. **Figure 85**
 94. **Figure 86**
 95. **Figure 87**
 96. **Figure 88**
 97. **Figure 89**
 98. **Figure 90**
 99. **Figure 91**
 100. **Figure 92**
 101. **Figure 93**
 102. **Figure 94**
 103. **Figure 95**
 104. **Figure 96**
 105. **Figure 97**
 106. **Figure 98**
 107. **Figure 99**
 108. **Figure 100**
 109. **Figure 101**
 110. **Figure 102**
 111. **Figure 103**
 112. **Figure 104**
 113. **Figure 105**
 114. **Figure 106**
 115. **Figure 107**
 116. **Figure 108**
 117. **Figure 109**
 118. **Figure 110**
 119. **Figure 111**
 120. **Figure 112**
 121. **Figure 113**
 122. **Figure 114**
 123. **Figure 115**
 124. **Figure 116**
 125. **Figure 117**
 126. **Figure 118**
 127. **Figure 119**
 128. **Figure 120**
 129. **Figure 121**
 130. **Figure 122**
 131. **Figure 123**
 132. **Figure 124**
 133. **Figure 125**
 134. **Figure 126**
 135. **Figure 127**
 136. **Figure 128**
 137. **Figure 129**
 138. **Figure 130**
 139. **Figure 131**
 140. **Figure 132**
 141. **Figure 133**
 142. **Figure 134**
 143. **Figure 135**
 144. **Figure 136**
 145. **Figure 137**
 146. **Figure 138**
 147. **Figure 139**
 148. **Figure 140**
 149. **Figure 141**
 150. **Figure 142**
 151. **Figure 143**
 152. **Figure 144**
 153. **Figure 145**
 154. **Figure 146**
 155. **Figure 147**
 156. **Figure 148**
 157. **Figure 149**
 158. **Figure 150**
 159. **Figure 151**
 160. **Figure 152**
 161. **Figure 153**
 162. **Figure 154**
 163. **Figure 155**
 164. **Figure 156**
 165. **Figure 157**
 166. **Figure 158**
 167. **Figure 159**
 168. **Figure 160**
 169. **Figure 161**
 170. **Figure 162**
 171. **Figure 163**
 172. **Figure 164**
 173. **Figure 165**
 174. **Figure 166**
 175. **Figure 167**
 176. **Figure 168**
 177. **Figure 169**
 178. **Figure 170**
 179. **Figure 171**
 180. **Figure 172**
 181. **Figure 173**
 182. **Figure 174**
 183. **Figure 175**
 184. **Figure 176**
 185. **Figure 177**
 186. **Figure 178**
 187. **Figure 179**
 188. **Figure 180**
 189. **Figure 181**
 190. **Figure 182**
 191. **Figure 183**
 192. **Figure 184**
 193. **Figure 185**
 194. **Figure 186**
 195. **Figure 187**
 196. **Figure 188**
 197. **Figure 189**
 198. **Figure 190**
 199. **Figure 191**
 200. **Figure 192**
 201. **Figure 193**
 202. **Figure 194**
 203. **Figure 195**
 204. **Figure 196**
 205. **Figure 197**
 206. **Figure 198**
 207. **Figure 199**
 208. **Figure 200**
 209. **Figure 201**
 210. **Figure 202**
 211. **Figure 203**
 212. **Figure 204**
 213. **Figure 205**
 214. **Figure 206**
 215. **Figure 207**
 216. **Figure 208**
 217. **Figure 209**

ABSTRACT

A method for removing organometallic and organosilicate residues remaining after a dry etch process from semiconductor substrates. The substrate is exposed to a conditioning solution of a fluorine source, a non-aqueous solvent, a complementary acid, and a surface passivation agent. The fluorine source is typically hydrofluoric acid. The non-aqueous solvent is typically a polyhydric alcohol such as propylene glycol. The complementary acid is typically either phosphoric acid or hydrochloric acid. The surface passivation agent is typically a carboxylic acid such as citric acid. Exposing the substrate to the conditioning solution removes the remaining dry etch residues while minimizing removal of material from desired substrate features.

20

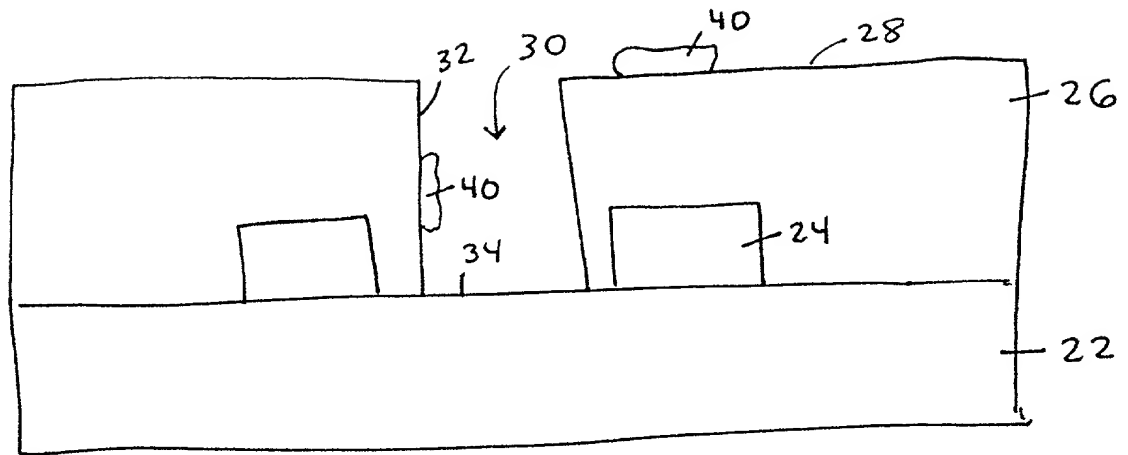


FIG. 1

20

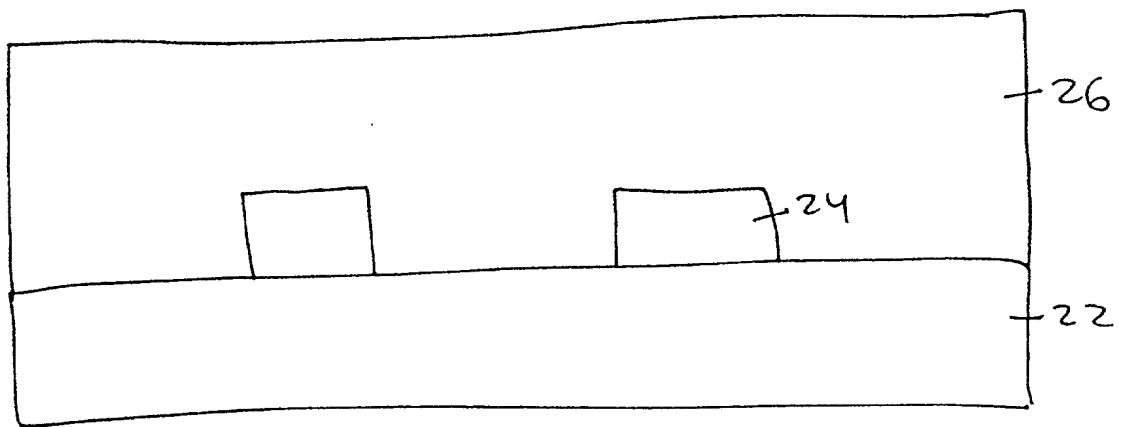


FIG. 2

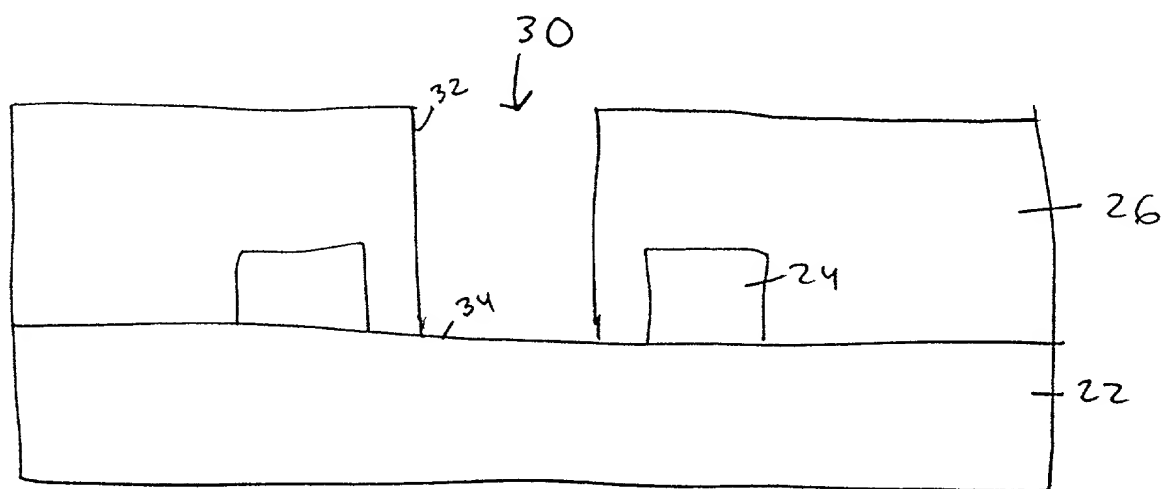


FIG. 5

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

ACID BLEND FOR REMOVING ETCH RESIDUE

The specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by an amendment, if any, specifically referred to in this oath or declaration.

I acknowledge the duty to disclose all information known to me which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Not Claimed
_____ (Number)	_____ (Country)	_____ (Filing Date)	<input type="checkbox"/>
_____ (Number)	_____ (Country)	_____ (Filing Date)	<input type="checkbox"/>
_____ (Number)	_____ (Country)	_____ (Filing Date)	<input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, § 120/365 of any United States and PCT international application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56(a) which became available between the filing date of the prior application and the national or PCT international filing date of this application:

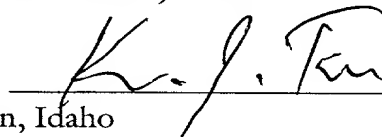
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Please address all correspondence to Thomas J. D'Amico of Dickstein Shapiro Morin & Oshinsky LLP located at 2101 L Street NW, Washington, DC 20037-1526. Telephone calls should be made to (202) 785-9700.

Full name of first inventor: Kevin J. Torek

Inventor's signature:



Date:

6/24/99

Residence: Meridian, Idaho

Citizenship: United States of America

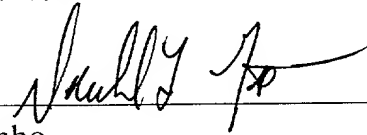
Post Office Address: 1718 N. Kastle Falls Avenue
Meridian, ID 83642

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
DECLARATION FOR PATENT APPLICATION

Signature Page for Second Inventor

Full name of second inventor: Donald L. Yates

Inventor's signature:



Date:

6/24/99

Residence: Boise, Idaho

Citizenship: United States of America

Post Office Address: 11151 Musket Street
Boise, ID 83713

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Kevin J. Torek et al.

Serial No.: Not Yet Assigned

Group Art Unit: Not Yet Assigned

Filed: Concurrently Herewith

Examiner: Not Yet Assigned

For: ACID BLEND FOR
REMOVING ETCH RESIDUE

Assistant Commissioner for Patents
Washington, D.C. 20231

**POWER OF ATTORNEY BY ASSIGNEE AND
CERTIFICATE BY ASSIGNEE UNDER 37 CFR § 3.73(b)**

Micron Technology, Inc., assignee of the entire right, title and interest in the above-identified application by virtue of the assignment attached hereto (which is also being submitted concurrently for recordation), hereby appoints the attorneys and agents of the firm of Dickstein Shapiro Morin & Oshinsky LLP located at 2101 L Street NW, Washington DC 20037-1526, listed as follows: Gary M. Hoffman, 26,411; Thomas J. D'Amico, 28,371; Donald A. Gregory, 28,954; James W. Brady, Jr., 32,115; Jon D. Grossman, 32,699; Mark J. Thronson, 33,082; Laurence E. Fisher, 37,131; John R. Fuisz, 37,327; Brian A. Lemm, 43,748; Gianni Minutoli, 41,198; Eric Oliver, 35,307; William E. Powell, III, 39,803; James M. Silbermann, 40,413, and also attorneys of Micron Technology, Inc. as its attorneys with full power of substitution to prosecute this application and to transact all business in the Patent and Trademark Office in connection therewith.

The assignee certifies that the above-identified assignment has been reviewed and to the best of the assignee's knowledge and belief, title is in the assignee.

Dated: Feb 24, 1999